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**Some Physical Properties
of Paint, Varnish and
Nitro-Cellulose
Lacquer Films**



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Some Physical Properties of Paint, Varnish and Nitro-Cellulose Lacquer Films

By

Harley A. Nelson, M.A.

Chief of Pigment Research Division
The New Jersey Zinc Company

and

George W. Rundle

Investigator, Research Division
The New Jersey Zinc Company



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THE information published in this Research Bulletin has been derived in part from the following reports previously presented before the American Society for Testing Materials and published in the Proceedings of that Society.

"Stress-Strain Measurements on Films of Drying Oils, Paints and Varnishes" by H. A. Nelson. Proceeding, Am. Soc. Testing Mats., Vol. 21, p.-1111 (1921).

"Further Studies of the Physical Properties of Drying Oil, Paint and Varnish Films," by H. A. Nelson and G. W. Rundle. Proceedings Am. Soc. Testing Mats., Vol. 23, Part II, 1923.

"Physical Properties of Varnish Films Indicated by Stress-Strain Measurements," by H. A. Nelson. Proceedings, Am. Soc. Testing Mats., Vol. 23, Part I, 1923.

"The Study of Nitrocellulose Lacquers by the Stress-Strain Method," by G. W. Rundle and W. C. Norris. Proceedings, Am. Soc. Testing Mats., Vol. 26, Part II, 1926.

INTRODUCTION

A paint, varnish or lacquer gives protection in proportion as it retains certain desirable properties despite the action of the weathering agents to which it is exposed. There may be argument as to just what properties are desirable, but there is no question as to the desirability at all times of a proper balance between elasticity and tensile strength, or a certain degree of toughness, retained over a maximum period of time. Hence, the development of rapid and easy methods for measuring by some empirical means, and a detailed study of these stress-strain properties under all conditions, must be considered necessary in the development of the paint, varnish and allied industries.

Measurements of the stress-strain properties on films of paint are first referred to in connection with the Atlantic City and Pittsburgh Paint Test Fences,¹ and later described more fully by Gardner.² The instrument used, known as the Perry Filmometer, recorded the weight of mercury required to rupture a film of paint clamped between two rings, and measured the expansion of the film under this pressure.

FILMS FOR TESTING PURPOSES

In the experiments that follow, films for testing have been obtained by painting, spraying or flowing the material on a tinned surface which has been previously amalgamated with mercury. Ordinary roofing tin can be used, the only requirements being a smooth surface and freedom from pinholes. Or clean sheet iron itself may be surfaced with the tin amalgam by rubbing on along with the amalgam, a small amount of dilute hydrochloric acid. The wet coating adheres very well to such surfaces, and, when dry, is easily removed without any forcing or distortion.

The method of applying the film must be suited to the material under study. If the consistency is proper for spraying, this produces a very

¹Laboratory Study of Panels of Atlantic City and Pittsburgh Test Fences, Bulletin No. 19, Scientific Section, Paint Mfg. Assoc.

²H. A. Gardner, "Paint Technology and Tests," 1911.

uniform film, whether done in one or more coats. Brushing on of paint is unsatisfactory, unless the "yield value" is low enough to permit the brush marks to flow out. Lacquers, lacquer enamels as well as varnishes and oleoresinous enamels of high vehicle content are most easily flowed, and generally yield very satisfactory film specimens.

No absolute means have been found for controlling the thickness of film specimens, and producing films of a definite thickness resolves itself to a matter of "cut and try" depending on the skill and experience of the operator. A suitable working range for paint is a thickness of from 0.120 to 0.150 mm. Varnishes, lacquers and lacquer enamels can usually be best manipulated to yield films ranging from 0.090 to 0.100 mm. in thickness. It is important that for any one comparative test, the thickness of the specimens be kept nearly equal, and certain allowances made for unavoidable differences. These will be discussed later.

The coated amalgamated panel is dried and aged under reproducible and constant conditions of temperature and relative humidity. At least 24 hours before testing, the film is stripped from the panel, cut into test specimens, the thickness determined and noted on each specimen. The thickness is determined as the average of about five readings taken along the length of the constricted area.

In order to determine the variations due to humidity and absorbed moisture, a scheme of desiccation and humidification has been adopted. This consists of putting duplicate test specimens in a desiccator over concentrated sulfuric acid and in humidors maintained at 30%, 60% and 80% relative humidities at least 24 hours before the test specimens are to be tested.

APPARATUS AND PROCEDURE

The Tension Apparatus¹

The ordinary helical spring, tempered to follow Hooke's law, is ideal for application of the small loads that often must be used. By having at hand a number of these springs of varying strengths, the operator has a wide range for variations in the rate at which the load is applied.

It is on this basis that the instrument shown in Figure 1 was developed. The power is supplied at the base by a $\frac{1}{16}$ h.p. motor connected with a slid-

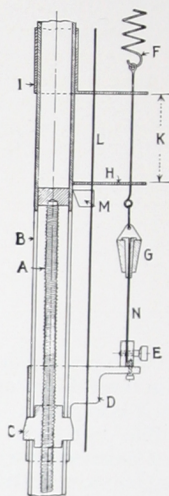


FIGURE 1
Tension Apparatus

¹This apparatus was designed primarily as a research instrument of great flexibility. It can be used equally well for testing linseed oil films having little strength and great flexibility or nitrocellulose films having great strength and small distensibility. Since this instrument has been in use, other instruments of simpler design have been developed, notably that described by H. A. Gardner, Circular No. 240 Scientific Section, Paint Mfg. Assoc. Commercial Stress-Strain machines are also available that are satisfactory.

Note: Walker and Thompson have used and recommended a spinning disk method for producing uniform films of known weight and thickness. A. S. T. M. Proceedings Vol. XXII, Part II, page 464, 484, 1922.

ing rheostat to provide a range of speeds. The screw *A* is fitted in the center of the hollow main standard *B*, and driven through a worm reduction gear to the motor. The standard is slotted over a greater part of its length to permit the split-nut *C*, actuated by the screw, to drive the moving platform *D*. Opening the split-nut permits free adjustment of the moving platform to any desired position. On this platform are mounted the lower grip *E*, for holding the specimen, and the extensometer attachment (shown in Figure 2), both of which are detachable. The spiral spring *F* is so sus-

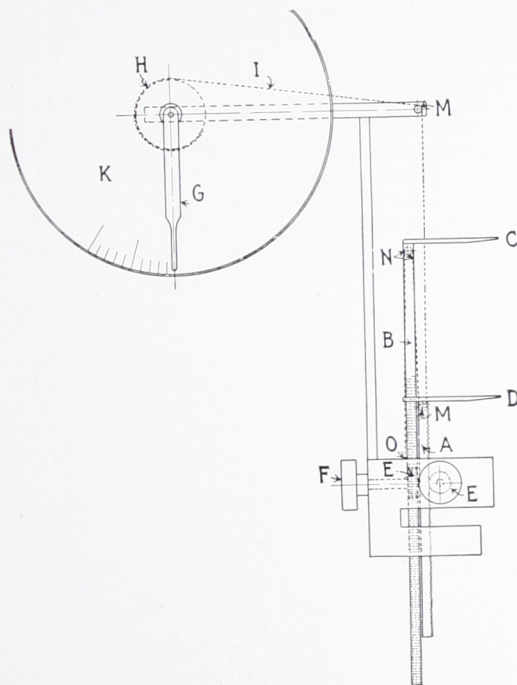


FIGURE 2—Extensometer Attachment

ended that it is in alignment with the lower grip, and to it is attached, by a long wire hook, an aluminum grip *G*. The wire hook is provided with a stop *H*, which is caught by the sliding sleeve *I*. This sleeve follows the movable platform at a distance determined by an adjustable hook. It is evident that the distance *K* between this sliding sleeve and the stop on the wire hook must take care of the elongation of the specimen, and the length of the wire hook must be calculated accordingly. A taut brass rod *L*, one-sixteenth of an inch in diameter, extends the full length of the instrument. On this rod is a celluloid marker *M*, which moves down with

H, and, when the break occurs, remains fixed to indicate the ultimate load, the spring having been previously calibrated in grams according to the millimeter scale etched on the side of the standard *B*.

The Extensometer

The extensometer attachment shown in Figure 2 is mounted on the movable platform. It consists of two movable racks (*A* and *B*) carrying the pointers *C* and *D* and actuated by the pinions *E* and the thumb screws *F*. Reading the instrument is facilitated by the indicator *G* mounted on a shaft extending to the small drum (*H*) back of the dial *K*. A strong silk cord *L* is wound on the drum and passes over the pulley *M* in line with the very small pulley *N* mounted on the back of the rack *A*. Thence, it passes up and over a similar pulley *N* on the rack *B*, and finally down to be fastened at *O*. The compensating action of this cord renders the indicator very sensitive to any changes in the distance between the two pointers, which are set at predetermined points on the test specimens. The dial is calibrated to read directly the percentage of the original distance between these marks represented by the elongation. A penciling device mounted on the indicator and automatically actuated by a small electro-magnet at every increment in load, facilitates taking successive readings when a complete stress-strain diagram is wanted.

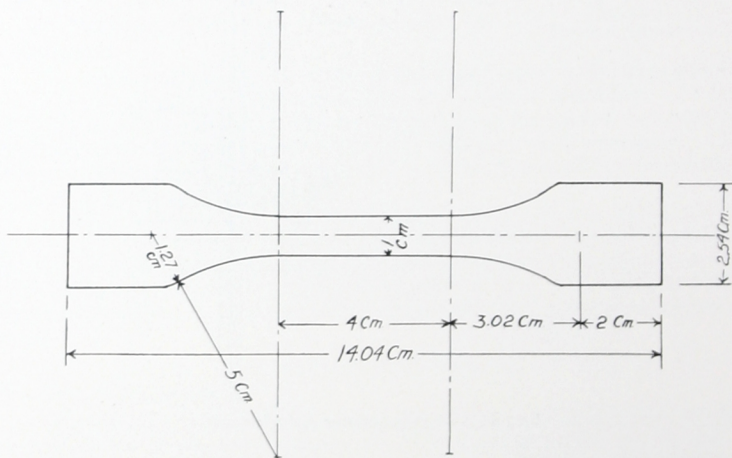


FIGURE 3
Form and Dimensions of Test Specimen

The Grips

The upper grip *G* (Figure 1) is made of cast aluminum, and grips the samples between two wedge-shape sections, which are forced into a similar opening in the center of the block. The lower grip *E* is made of brass. Each jaw of the latter is covered with rubber in order to protect the specimen from any localized pressure of sharp edges.

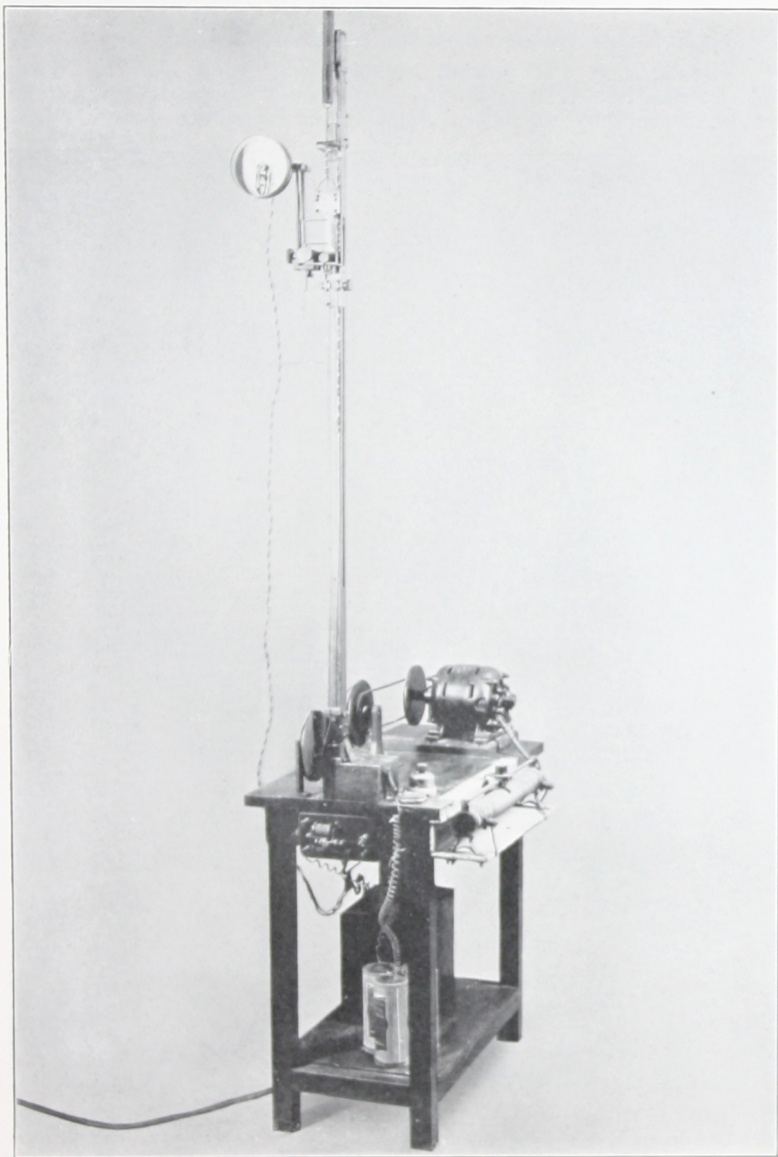


FIGURE 4

Stress-Strain Apparatus Complete¹ with Extensometer and Test Specimen in Position for a Test.

The Die for Cutting Test Specimens

The die selected for cutting test specimens, shown in Figure 3, was modeled after that recommended by the Bureau of Standards for use in the testing of rubber,¹ with such modifications in dimensions as were found

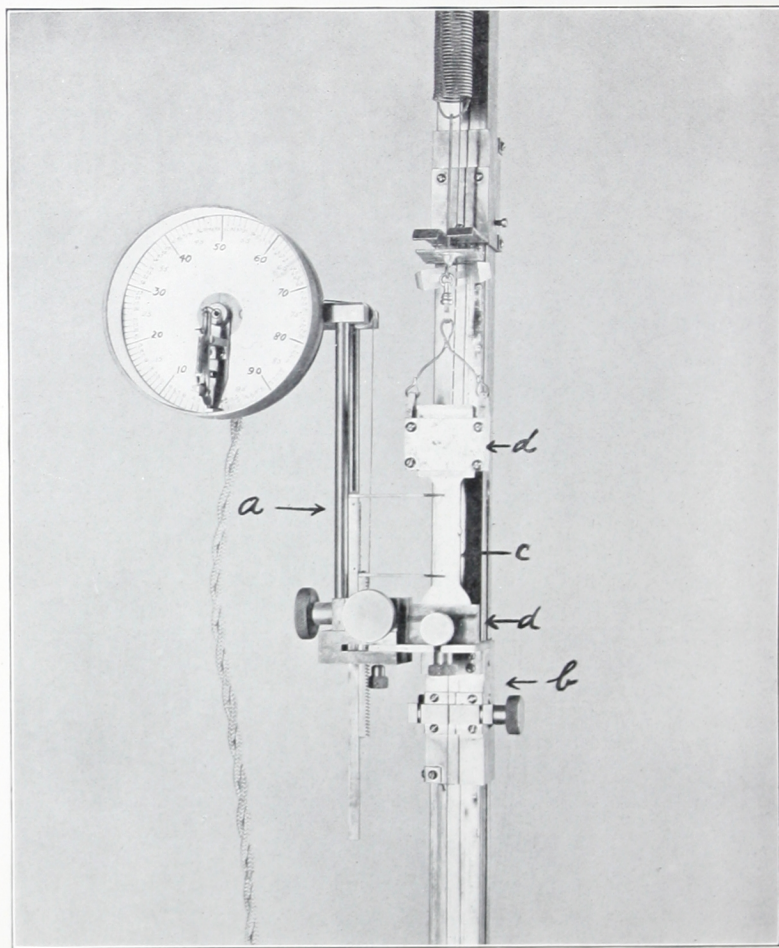


FIGURE 5

Detail of Extensometer (a) mounted on moving platform (b). Specimen (c) mounted in clamps (d) ready for beginning a test.

¹Circular No. 38, U. S. Bureau of Standards.

Also see discussion that follows under section on *Dimensions of Test Specimens*.

practicable. It should be made of tool-steel, carefully sharpened, and free from ragged edges, as the cut must be clean as possible. Mounting the die in an Arbor press is very satisfactory. The cutting is done against a maple wood block, over which is laid a piece of ordinary cardboard. A strip of writing paper serves as a background for the film to facilitate handling and prevent possible injury.

The Procedure During a Test

Figure 4 shows the apparatus complete and ready for a test. Briefly stated, the procedure during a test is as follows: The test specimen is taken from the desiccator or humidor and quickly fitted into the upper grip, which is hung on the hook attached to the spring, and the moving platform adjusted to bring the lower grip into position. The alignment of the test specimen with the grips and spring should be as nearly perfect as possible. The extensometer is then fitted into its place on the platform, and the indicator set at the "zero" per cent mark. The pointers then indicate the places for the markings on the test specimen, for which two small

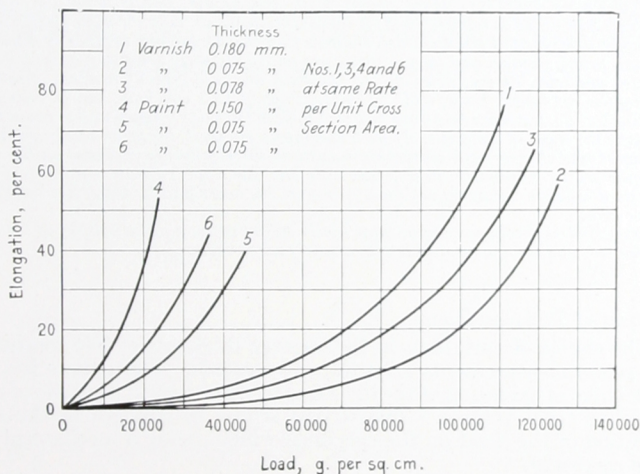


FIGURE 6
Effect of Thickness of Film and Rate of Applying Load

dots made with ink will suffice (heavy markings with pen or pencil must be avoided). The sliding sleeve, which acts as a stop, is adjusted to the desired height, the rheostat of the motor adjusted to give the desired rate of loading, and the power finally applied by closing the split-nut on the moving platform. When the rupture occurs, the celluloid marker remains fixed to indicate the ultimate load.

Sufficient specimens should be measured to obtain check results. Four are usually sufficient. It is usually the case that the curves coincide but

vary more or less as to the ultimate breaking point. This is due, generally, to unavoidable minute flaws along the edges of the test specimen. It is permissible in this case to choose the curve which shows the greatest load.

FACTORS THAT INFLUENCE RESULTS

Dimensions of Test Specimens

The dimensions indicated in Figure 3 were chosen after experimenting with dies of various lengths and widths. The length, 4 cm., between marks on the constricted area, is convenient and suffices for the accuracy required. The width of 1 cm. was accepted because of the added convenience of a unit width in making calculations. Repeated observations have indicated, moreover, that the width of the test specimen is not a factor in the numerical results of a test, provided the rate at which the load is applied be calculated to the same number of grams per square centimeter of cross-sectional area per minute.

IMPORTANT NOTE: *More recent work comparing results with the constricted (dumb-bell) type of test specimen, used for these investigations, with the more simple rectangular (straight-side) type of test specimen indicate that the elongations ordinarily dealt with in testing oil, paint, varnish and lacquer films are not sufficiently great to require the use of a constricted specimen except, possibly, for the most accurate type of research investigation. A rectangular specimen, 1 cm. wide by approximately 12.5 cm. long, can be recommended for routine testing, but more care must be taken to keep the grips aligned and to avoid localized pressure by the edges of the grips. If such specimens are used, the grips can be set 4 cm. (or more) apart and the per cent elongation measured directly by the increase in the distance between the grips. Obviously, in this case only one (the upper) pointer on the extensometer need be used to follow the motion of the upper grip, the lower pointer being fixed at the top of the lower grip.*

Rectangular test specimens can be most easily cut by using a metal templet of the size and shape desired, and tracing around it with a safety razor blade.
Feb. 13, 1930

Thickness of Test Specimens

The effects of variations in the average thickness of test specimens on stress-strain measurements arise from two causes. First, there is a difference in stage of oxidation of the films due to variations in the ratio of surface exposed to total volume. The second is due to changes in the rate of application of the load on the specimen which, being a mechanical effect, can be corrected.

In Figure 6, curves Nos. 1 and 2 represent two sections of a spar varnish film treated similarly throughout, of average thicknesses 0.180 and 0.075 mm. respectively. Curves Nos. 4 and 5 are of an ordinary combination paint, the films being 0.150 and 0.075 mm. average thickness, respectively. All of these curves were taken at the same grip speed. Curves Nos. 3 and 6, however, were taken after adjusting the grip speed for the thinner specimens so that the calculated rate in grams per unit cross-sectional area per minute is the same as that for the thicker specimen, or 15,000 g. per sq. cm. per min. Obviously, the differences between Nos. 1 and 3 or Nos. 4 and 6 are due to differences in the stages of oxidation attained by the specimens, but the variations between Nos. 2 and 3 or Nos. 5 and 6 can be avoided by proper adjustment of the grip speed.

Rate at Which Load is Applied

According to the curves in Figure 7 this test, when applied to oxidizing films, has the fault common to all dynamic tests on ordinary materials, namely, a variation in results with changes in the rate at which the load is applied. The rates of loading are calculated to the number of grams applied per unit cross-sectional area per minute.

Table I summarizes one of the several tests further illustrating the effect of variations in the rate of applying the load.

TABLE I—EFFECT OF RATE OF APPLYING LOAD

Film.	Rate, G. per Sq. Cm. per Min.	Elongation, Per Cent.	Tensile Strength, G. per Sq. Cm.
Paint	100	23	38 700
Paint	13 400	19	42 700
Paint	47 000	17	49 500
Paint	52 000	15	49 000
Paint	60 000	15	49 000
Paint	2 000 000 <i>a</i>	..	82 000
Paint	2 000 000 <i>a</i>	..	79 000

This is in accord with what is generally found, namely (1) that the ultimate elongation varies inversely and (2) the ultimate tensile strength

a Calculated to about this figure from time required to apply full load by rapid jerk.

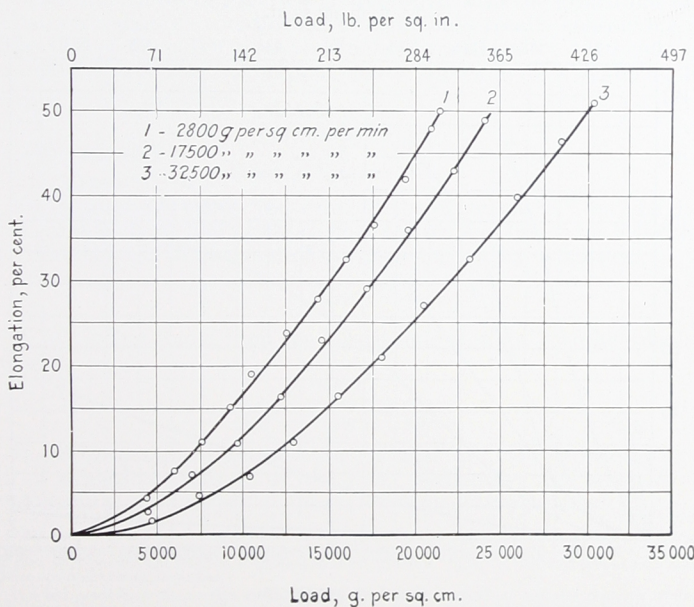


FIGURE 7
Effect of Change in Rate of Application of Load

varies directly as the rate of application of the load, when calculated to load per unit cross-sectional area per minute.

Adjustments of the rate of loading are facilitated by the calibrated rheostat connected with the driving motor. The thickness and probable elongation of the specimen being known (the latter, if more accuracy is desired, by a rapid preliminary test), the grip speed can then be adjusted so as to give a loading rate at some predetermined figure. A rate of 15,000 g. per sq. cm. per min. has been found to be an optimum rate for ordinary tests.

STUDY OF STRESS-STRAIN CURVES

Typical Forms of Curves

Films of various vehicle-pigment and vehicle-gum combinations have been studied with the object of finding the typical forms for the stress-strain curves of oxidizing films, and noting any similarities or dissimilarities. As paint and varnish mixtures have so often been referred to, in an off-hand way, as being similar to rubber in their properties, it was also interesting to determine just to what extent this holds true.

The curves in Figure 8 are plotted so as to bring into prominence the typical forms that have been observed. Curve No. 1 is that of a vulcanized

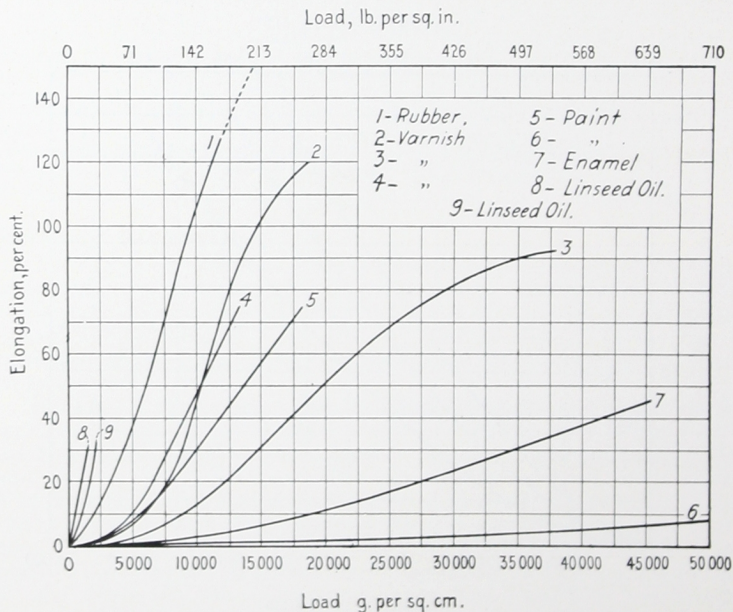


FIGURE 8
Typical Forms of Stress-Strain Curves

rubber, elongated barely to the point where the outward bend indicates increased resistance to distortion, thus exhibiting the characteristic S form¹. This portion of the curve is but a small part of the whole, the ultimate elongation and tensile strength on this sample being about 350 per cent and 1280 lb. per sq. in. (90,000 g. per sq. cm.) respectively.

Curves Nos. 2 and 3 are for films of two high-grade China wood oil varnishes recommended for exterior use under severe exposure. The samples were about two weeks old. No. 2 contained 45 per cent volatile and No. 3 contained 55 per cent volatile. No. 4 is of a common, fairly rapid drying, interior varnish about three days old, and is typical of this varnish and of several other linseed oil varnishes examined, although the ultimate points for others are often higher. No. 5 is of a soft film of paint, while No. 6 is the same paint after oxidation has been carried almost to the extreme by exposure to warm dry air. Curve No. 7 is typical of the best grade enamels examined after several months aging. Curves Nos. 8 and 9 are of kettle bodied linseed oil, No. 8 having been taken as soon as the film was sufficiently strong to permit handling, and No. 9 after about three months aging, part of the time at temperatures slightly above room temperature in order to hasten oxidation.

Mathematical Study of Typical Curves²

When the curves of Figure 8 are replotted with the logarithms of the stress-strain values as coordinates, straight lines result (considering only that portion of the curve up to the final outward bend.) Mathematically interpreted, this means the original curves approximate a parabolic form according to the equation:

$$y = ax^n$$

or in this case

$$\text{Strain} = \text{Factor} \times \text{Stress}^n$$

For a parabolic curve, the value of the exponent "n" may be determined graphically by finding the slope of the straight line of the logarithmic plot. This slope is the tangent of the angle "a" or, by definition,

$$\tan a = \frac{y}{x} = n$$

If "n" is first found from the logarithmic plot, "a" can be calculated as follows:

$$\begin{aligned} y &= ax^n \\ \log y &= \log a + n \log x \\ \log a &= \log y - n \log x \end{aligned}$$

In oxidizing films, the values for "n" and "a" vary depending on the stage of oxidation attained by the film. Generally, the value for "n" increases and the value for "a" decreases as oxidation progresses.

¹This outward bend (or S shape) of the curve has been observed to be characteristic of high-grade spar varnishes. Apparently, the more pronounced this outward bend appears (other conditions being equal) the better the varnish is suited to general outdoor exposure. That is, physical properties analogous to rubber are desirable in varnishes.

²It is not possible to discuss this subject adequately in this publication and the reader is referred to "Stress-Strain Measurements on Films of Drying Oils, Paints and Varnishes," by H. A. Nelson. Proceedings, Am. Soc. Testing Mats., Vol. 21, page 1111, or additional discussion of the mathematical curves and the probable meaning of the variations observed in the values for "n" and "a" as oxidation of the film progresses.

Ultimate Elongation and Tensile Strength

The amount of distortion to which a film will submit before rupturing entirely appears to be a characteristic property depending on the components of the film and the stage of oxidation, or deterioration and, therefore, cannot be considered to any extent apart from specific tests. Films of common paints and varnishes generally lose in ultimate elongation, and gain in tensile strength, as normal oxidation proceeds. But notable exceptions to this have been observed in the case of better grade varnishes, which will often hold a very constant ultimate elongation throughout a long period of oxidation, during which time the tensile strength increases steadily.

SOME FACTORS THAT INFLUENCE
THE DISTENSIBLE PROPERTIES OF OXIDIZING FILMS

Moisture

Some, or perhaps all, of the film constituents are more or less hygroscopic. The important role that absorbed moisture may play is graphically illustrated in Figure 9. The curves shown are for three single pigment paints (in a raw linseed oil, turpentine and dryer vehicle) aged 50 days at

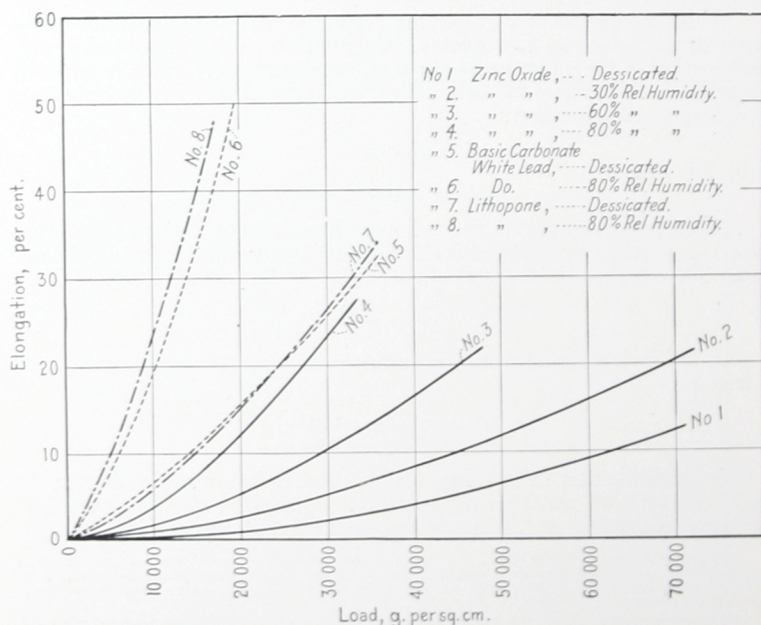


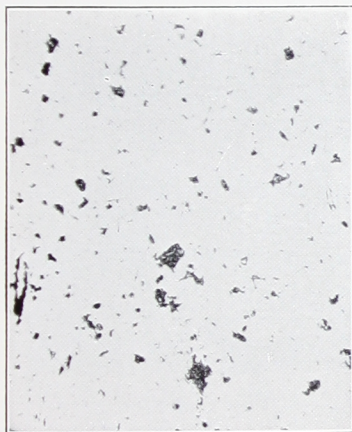
FIGURE 9
Effect of Absorbed Moisture on the Relative Positions of Stress-Strain Curves

35°C. previous to being tested. The specimens were exposed for 48 hours to atmospheres maintained at the desired relative humidities.

Reasons for the tendency to cracking of straight zinc oxide linseed oil paint in very dry exposures, and the very poor resistance to wear exhibited by basic carbonate white lead paints in humid localities, are evident from the relative positions of the curves.

There apparently is a connection between the so-called moisture resistance of films and the effect of moisture on the relative positions of the stress-strain curves.

Further study of the effects of absorbed moisture on stress-strain curves proved that the curves for varnish films follow the observed general rule for paint films, namely, that the distensibility varies directly, while the tensile strength varies inversely as the absorbed moisture content of the film.



(a) Freshly Oxidized Film. (Dark spots are dust particles on the surface).



(b) Film Exposed 13 Hours to Ultra-violet Light.

FIGURE 10

Photomicrographs of Linseed Oil Films, Stretched to Elongation of 10 per cent Above Original (X 60).

Ultra-Violet Radiations

It is interesting to note the photomicrographs shown as Figure 10. Figure 10 (a) is of a freshly oxidized film of oil. Figure 10 (b) is of the same film after 13 hours of accelerated oxidation under the ultra-violet light. When the photomicrographs were taken, each specimen was stretched 10 per cent over its original length. Note that (a) shows no visible signs of the distortion, but that (b) which is very resistant to slight distortion, disintegrates completely. Hence, its high initial resistance to distortion and the rapid up-sweep of its stress-strain curve once this initial resistance has been overcome. This is indicated by an abnormally high value $n=2.7$ in the mathematical formula for the curve.

Many schemes for accelerated weathering in which ultra-violet radiations from artificial sources are utilized to simulate the effects of sunlight have been described.¹ The reasons for the effects observed when films are

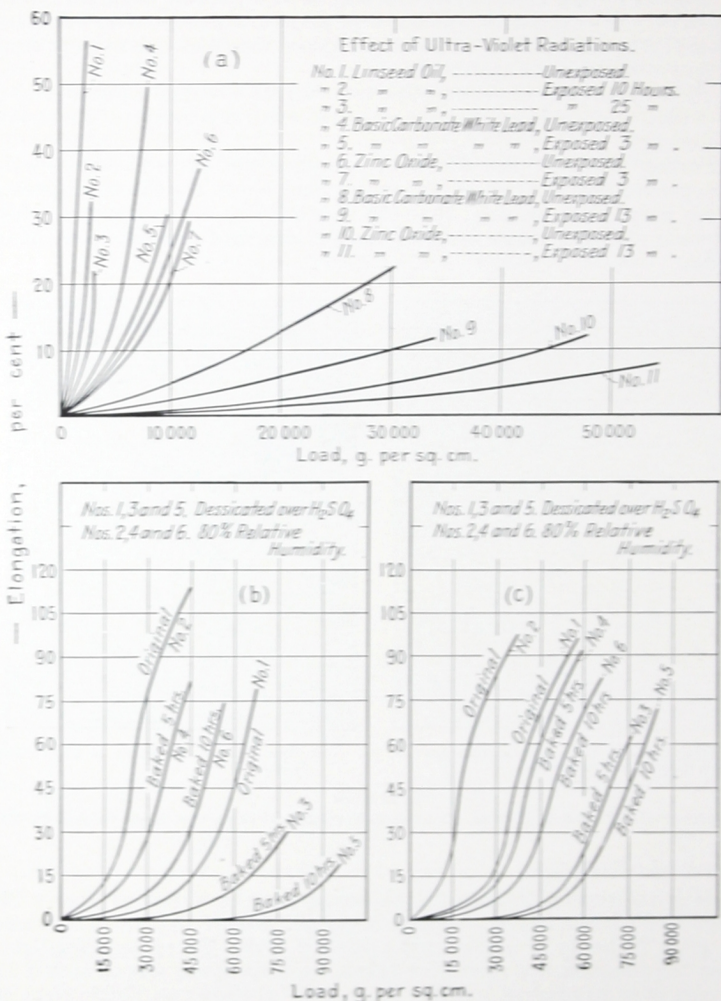


FIGURE 11

Typical Effects of Weathering Agents on the Properties of Films
(a) Effects of exposure to ultra-violet radiations; (b) and (c) Effects of exposure to heat

¹H. A. Nelson, "Accelerated Weathering of Paints on Wood and Metal Surfaces," Proceedings, Am. Soc. Testing Mats., Vol. 22, Part II, page 485 (1922).

exposed to ultra-violet light are demonstrated graphically in Figure 11 (a). Briefly, we may emphasize (1) the very great susceptibility of linseed oil alone; (2) the relative protection offered by an opaque (to ultra-violet radiations) pigment such as zinc oxide as against the other extreme, basic carbonate white lead, which is known to be more transparent to ultra-violet radiations.

The hardening, and subsequent disintegration of the surface linseed oil binder through reactions induced by ultra-violet radiations must be recognized as a fundamental cause for the failure of paints by chalking. Visible evidence of film deterioration as chalking may be hastened by temperature expansion and contraction effects, but chalking may be reproduced on pigments such as basic carbonate white lead by light exposure alone without introducing any temperature or moisture variations.

That zinc oxide and basic carbonate white lead do differ in the degree to which they transmit ultra-violet radiations is indicated in an interesting

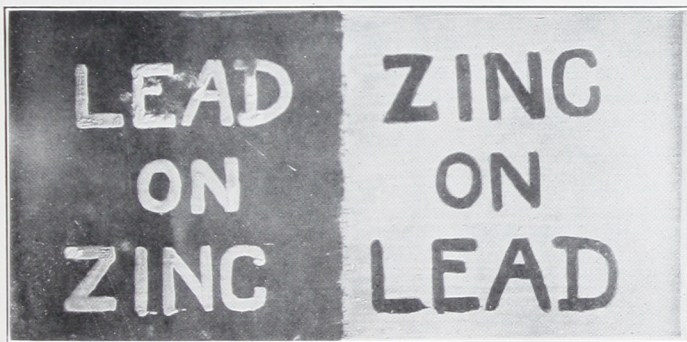


FIGURE 12

Photograph Taken by Reflected Light Radiations from the near Ultra-violet, Illustrating Differences in Transmission by Two Pigments

way in Figure 12. To the eye, the lettering and background are white and quite indistinguishable. Photographed¹ at an angle of 90° by reflected light from the near ultra-violet region of the spectrum (range about $\lambda = 3800 \text{ \AA. U.}$ to approximately $\lambda = 3100 \text{ \AA. U.}$) the zinc oxide reflected no radiations to activate the plate. Hence, the black photograph instead of white. The basic carbonate white lead reflected sufficient radiations to easily activate the plate and so appears an approximately normal white.

Reflected light from these surfaces would normally be possible only by transmission of the radiations from crystal to crystal and refraction during the course of this transmission until a certain portion finally emerges from the surface as reflected light. Obviously, then, one pigment has transmitted the radiations while the other has not.

¹By light from iron arc through Corning Glass G 586 A. W. Camera with crown-flint glass lenses

Heat

The immediate effect of increased temperature is to soften the film structure. No doubt this is due to a general increase in the mobility of the film constituents, or perhaps an increase of the liquid phase brought about by the melting of some otherwise solid material.

Naturally the reverse effect takes place at lower temperatures. The true extent of the loss of distensibility at low temperatures has not been accurately determined.

The well-known effects of continued application of heat are to hasten oxidation and polymerization. The most informing examples of how these may vary are those observed for varnishes. Figure 11 (b) represents a china wood oil-ester gum varnish with 30 gal. of oil to each 100 lb. of gum. The varnish used in the tests recorded in Figure 11 (c) has 40 gallons of china wood oil to each 100 lb. of ester gum. Of the curves shown, Nos. 1 and 2 are for the original films 35 days old; Nos. 3 and 4 after baking 5 hours at 95° C.; and Nos. 5 and 6 are for films after baking 10 hours at 95° C. Specimens Nos. 1, 3 and 5 have been desiccated over CaCl_2 and Nos. 2, 4 and 6 maintained at 80 per cent relative humidity for at least 48 hours just previous to testing. In this case, the decreasing effects of heat and moisture with increases in the oil content are evident.

Reaction Products (Soaps)

It is known that the characteristics of paint films are modified by soaps formed with acid vehicles. Figure 13 (a) illustrates the effect of increased zinc soaps on the zinc oxide paint film. It can be readily seen that even the differences between a vehicle of acid number 3 and one of acid number 6 would have a marked effect on the distensibility of the film when dry. This argues for vehicles of low acid number for use in zinc oxide paints.

It is to be expected that the plastic lead soaps would have the opposite effect, as indicated in Figure 13 (b). It also follows that very highly acid vehicles should be detrimental to lead paints used in regions of high relative humidity, since they tend to make the film excessively soft.

Addition of Hygroscopic Agents

The effect of absorbed moisture, shown in Figure 9 suggests the addition of materials more hygroscopic than the normal constituents of the film. For example, glycerol, which is quite hygroscopic, should normally be present in small amounts. If the amount present is increased by additions to the vehicle, decided softening results, as well as an increased effect of moisture. This last is illustrated by the wider spread of the curves as desiccated (Curves 1 and 3) and 80 per cent relative humidity (Curves 2 and 4) shown in Figure 13 (c).

The effect of moisture can be reversed by adding some material which is slightly hygroscopic, such as castor oil (Figure 13 d), although the total effect is to soften the film at lower humidities (Curve 3) due to an increase in the amount of non-oxidizing liquid phase present.

Generally, the distensibility of a film is determined by the mobile properties of the film constituents and the surface relationships between the several phases. The hygroscopicity of the film constituents will then be a determining factor in so far as the absorbed moisture affects the mobile properties or induces changes in the existing surface relationships.

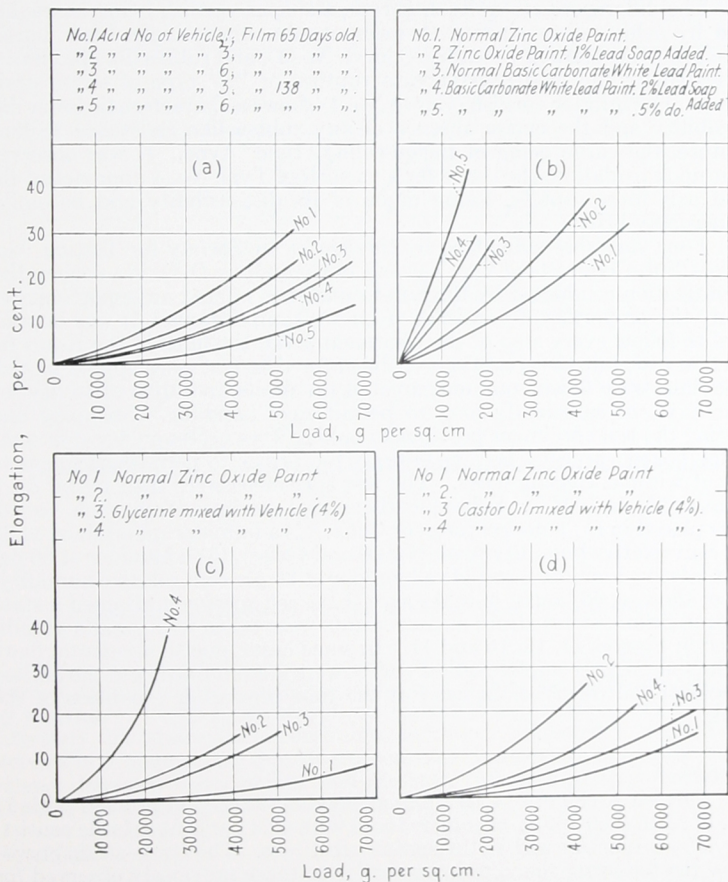


FIGURE 13

(a) and (b) Effects of the normal reaction products (soaps) formed in the film; (c) and (d) Effects of adding materials of varying degrees of hygroscopicity.

Note: In (c) and (d), Curves 1 and 3 are for desiccated films, while curves 2 and 4 were taken at 80 per cent relative humidity.

SOME APPLICATIONS OF STRESS-STRAIN METHODS IN STUDYING
THE PROPERTIES OF VARNISH FILMS

In Figure 8, Curves Nos. 2 and 3, are characteristic of high-grade spar varnishes designed for exterior exposures while Curve No. 4, is typical for a good grade of varnish as generally designed for interior exposures alone.

The differences are quite apparent, the spar varnish being characterized by a high distensibility throughout, an increasingly high tensile strength when allowed to oxidize (Curve No. 3), and rubber-like properties indicated by the final resistance to rupture or "S" type of stress-strain curve. The interior varnish (Curve No. 4) shows a characteristic lower distensibility and the entire absence of any rubber-like resistance to final rupture, the curve being of the so-called "rigid" type. It was observed that upon oxidation, the curve for a varnish of Type No. 4 approached the load axis more rapidly, losing much of its distensibility and becoming increasingly brittle.

Four varnishes submitted by the American Society for Testing Materials (Sub-Committee IX on Varnish, of Committee D-1)¹ in a cooperative investigation conducted by the Sub-Committee, offered an opportunity to study the properties of varnishes of known compositions. It was impractical to follow every step of the treatment given the films in the Kauri reduction test, but the conditions outlined for that test were approximated. The films were flowed on amalgamated tin sheets and allowed to dry for four days, or sufficiently long to permit easy handling. Stripping and cutting the test specimens previous to baking were necessary because some of the baked varnishes became entirely too brittle to permit specimens to be cut without causing flaws. The test specimens were then baked for 5 hours at 95° to 100° C. Subsequently several specimens from each varnish were placed in (1) a desiccator over CaCl_2 , (2) a humidor maintained at 30 per cent relative humidity (over H_2SO_4 and water), (3) a humidor at 60 per cent relative humidity, and (4) a humidor at 80 per cent relative humidity. After allowing 48 hours, to make sure that each specimen attained a state of equilibrium, stress-strain measurements were taken with results as indicated in Figures 14, 15, 16 and 17. In some cases, due to accidental flaws in the specimens, complete sets of curves were not obtained, and the limited supply of the varnishes on hand at the time prevented repetition of the work.

Varnish A

Varnish A (Figure 14) is a China wood oil-ester gum product with 27 gal. of oil to each 100 lb. of gum, reduced with 47.4 per cent volatile consisting of $\frac{1}{2}$ turpentine and $\frac{1}{2}$ turpentine substitute. The stress-strain curves show the following characteristics similar to those previously observed for spar varnishes:

1. High distensibility, which is affected only to a slight extent by changes in the absorbed moisture content of the film.

¹See report submitted to the Sub-Committee (IX) on Varnish and published as an appendix in the 1923 report of Committee D-1 on Preservative Coatings for Structural Materials, Proceedings A. S. T. M. Vol. 23, Part I, 1923 page 273-281.

2. High tensile strength, which is properly balanced by a well-maintained high distensibility, thus keeping the stress-strain curves centrally located in the plot.

3. A very pronounced resistance to final rupture, indicating a decidedly tough, rubber-like structure.

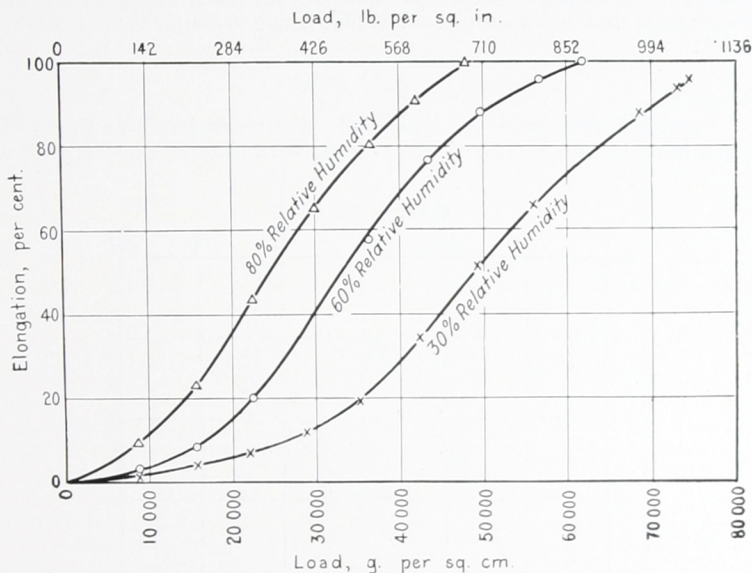


FIGURE 14
Stress-Strain Curves for Varnish A, China Wood Oil-Ester Gum

From these considerations certain results may be expected with this varnish upon exposure. In the first place, it should not be easily affected by moisture. Further, we would not expect this varnish to crack under extremely dry atmospheric conditions, nor when subjected to violent expansion and contraction due to temperature changes. Finally, the good balance between distensibility and strength indicates a tough material, which is not easily abraded and retains its gloss.

Varnish B

Varnish B (Figure 15) is a linseed oil-Kauri gum product with 27 gal. of oil to each 100 lb. of gum, reduced with 52.7 per cent volatile consisting of $\frac{1}{2}$ turpentine and $\frac{1}{2}$ turpentine substitute. This varnish shows the following characteristics:

1. A fairly high distensibility which varies only slightly with the moisture content of the film.

2. A fairly high tensile strength which, with the distensibility, gives a well-balanced curve centrally located on the plot.

3. Some resistance to final rupture as evidenced by the final outward swing of the curves.

We would expect this varnish to be comparatively unaffected by moisture or moisture changes. Its tendency to crack might be slightly greater than that of Varnish A. The film is not so tough as that of Varnish A.

Varnish C

Varnish C (Figure 16) is a linseed oil—lime-treated rosin product with 27 gal. of oil to each 100 lb. of gum reduced with 45.6 per cent turpentine

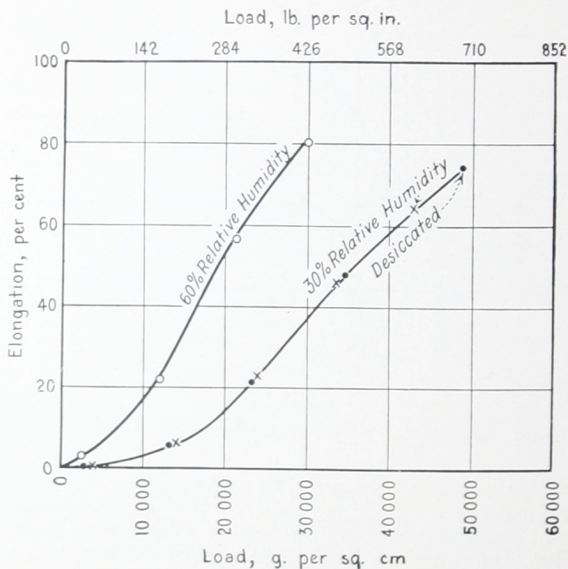


FIGURE 15
Stress-Strain Curves for Varnish B, Linseed Oil—Kauri Gum

substitute. In this varnish we have an entirely different product from any previously considered, as indicated by the following characteristics of the curves:

1. The distensibility varies tremendously with changes in moisture content of the film.

2. The tensile strength is only moderately high and the curves are well balanced only at intermediate humidities.

3. The film displays a certain amount of resistance to rupture at intermediate humidities, but loses this evidence of toughness at both high and low humidities.

This is distinctly not a varnish for out-door exposures. It would be badly affected by moisture and moisture changes. In dry climates, subject

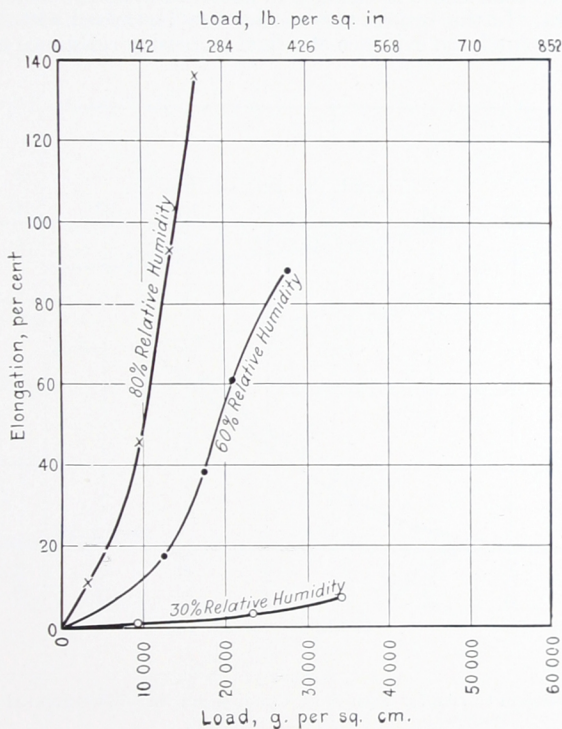


FIGURE 16
Stress-Strain Curves for Varnish C, Linseed Oil—Lime-Treated Rosin

to severe temperature variations, we would expect it to crack. On the other hand, if exposed at certain uniformly maintained humidities, it should give service, as indicated by the well-balanced curves at 60 per cent relative humidity.

Varnish D

Varnish D (Figure 17) is a China wood oil—lime-treated rosin varnish with 27 gal. of oil to each 100 lb. of gum, and reduced with 45.4 per cent turpentine substitute. This varnish also has distinct characteristics:

1. Very low distensibility even at high humidities.
2. High tensile strength which, with the low distensibility, gives a poorly balanced curve.
3. The total effect of changes in absorbed moisture content is relatively slight. In this respect the varnish may be classed with Varnish A.
4. Absolutely no evidence of a final increasing resistance to rupture.

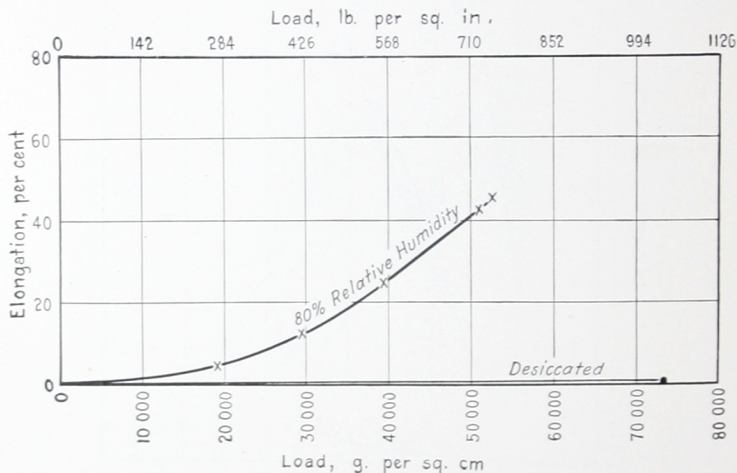


FIGURE 17
Stress-Strain Curves for Varnish D, China Wood Oil—Lime-Treated Rosin

We would expect this varnish to resist uniformly wet conditions well, but any variations from moist to dry exposure conditions would result in cracking. Because of the brittleness of the film, scratches might be expected to show more than, for example, on Varnishes A or B. Under moist conditions or very uniform conditions, its retention of gloss should be quite satisfactory.

EFFECT OF ADSORBED MOISTURE ON OTHER DISTENSIBILITY TESTS

The very pronounced effect of adsorbed moisture on the distensibilities of varnishes suggests that care in maintaining a uniform relative humidity during the period just before Kauri reduction test plates are bent, would be essential for accurate and comparable results. Quite possibly for such Varnishes as A, B and D, the errors introduced by humidity variations would be moderate, but it is apparent that even small variations in humidity might cause appreciable errors in testing a varnish which has its distensibility greatly affected by the adsorbed moisture content, as does Varnish C.

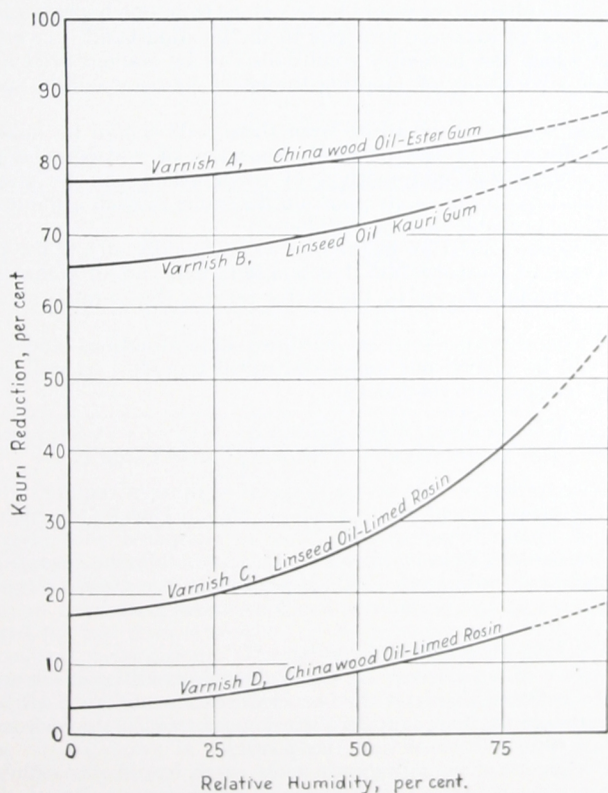


FIGURE 18
Effect of Relative Humidity During Final Cooling Period
on Kauri Reduction Test Values

Experiments further prove that the relative humidity to which the baked varnishes are exposed during the hour after baking and just prior to the bending test may have a pronounced effect on the results of the Kauri reduction test.

This is shown graphically in Figure 18. In drawing these curves, the true cracking points have been approximated from the extent of the cracking observed on each panel. It will be noted that the results are in close agreement with what is predicted by the stress-strain curves.

Obviously, if the Kauri reduction test is to be universally applied, controlled humidity conditions are essential during the period just prior to the bending test. Availability and ease of manipulation recommend the common method of desiccation over CaCl_2 .

A possible alternative would be to reduce from one hour to a few minutes the period of exposure previous to the bending test. In view of the ease with which the humidity conditions can be standardized and controlled, the advisability of adopting the latter course would be subject to question.

Certain general observations from these tests should be emphasized:

1. Differences in the physical properties of varnishes, depending on their composition and method of preparation, can be graphically demonstrated by means of stress-strain diagrams in such a manner as to indicate their probable field of usefulness.

2. Adsorbed moisture in the film so profoundly affects the physical characteristics of a varnish film that humidity and humidity changes may be the determining factor in the useful service the varnish gives upon exposure.

3. Physical tests, such as hardness determinations and cracking tests, should be carried out under controlled humidity as well as under controlled temperature conditions.

SOME APPLICATIONS OF STRESS-STRAIN METHODS IN STUDYING THE PROPERTIES OF NITROCELLULOSE LACQUERS

Heavier springs are the only additional equipment required over that used in the measurement of oleoresinous films. Due to the high tensile strength of nitrocellulose lacquer films, as compared with oleoresinous films, it is necessary to use a higher loading rate. For the average lacquer film a convenient loading rate is 50 kg. per sq. cm. per minute, as compared with 15 kg. per sq. cm. per minute for oleoresinous materials.

Influence of Temperature and Humidity

The effect of temperature on the distensible qualities of nitrocellulose lacquers is, in general, greater than on oleoresinous materials. It is advisable to maintain the temperature of the room in which the measurements are made within as narrow limits as possible.

The influence of humidity is, in most cases, less in nitrocellulose lacquers than on oleoresinous materials. The hygroscopicity of the constituents is, of course, the most important factor. The kind and amount of gums used exert a considerable influence. The effect of humidity in a few different lacquers containing various resins is pointed out in the curves of Figure 23.

Influence of Film Thickness

As mentioned above, the specimens are classified according to average thickness when they are cut. It is desirable to compare only films of nearly the same thickness for two reasons.

The first reason is one of expediency only. To maintain a constant loading rate with films differing widely in thickness, it is necessary to use springs of different values and adjust the speed. It is obviously much more convenient to use one spring and slightly varying speeds throughout a given series of tests.

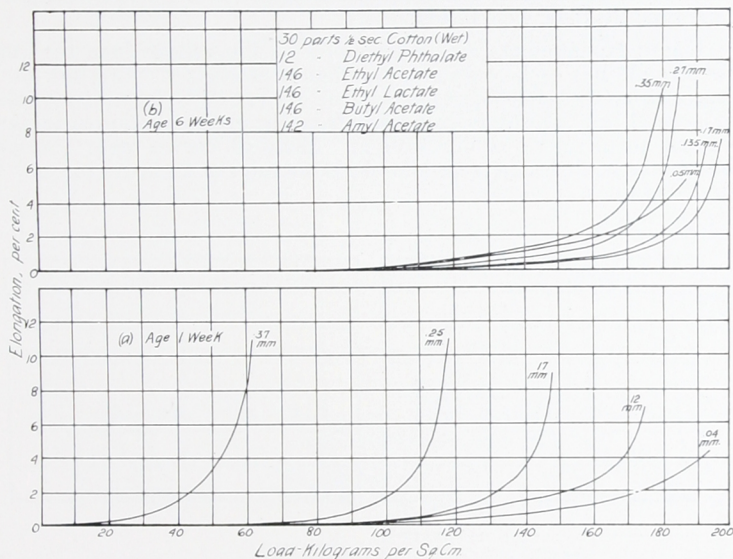


FIGURE 19
Influence of Film Thickness on the Retention of Volatile Matter

The second reason for using films of approximately the same thickness is because of retention of volatile matter by a film. This has been found to be quite an important factor in the measurements of lacquer films that have aged for less than a week or for even longer periods in the case of certain solvent compositions. The two main factors in the degree of volatile retention are film thickness and nature of solvents used. Considering a series of the same solvent composition the films should be of approximately the same thickness if tests are to be run within a week or two after flowing.

The curves shown in Figure 19 clearly illustrate the erroneous conclusions one is liable to draw when comparing films differing widely in thickness. It is true that the solvent mixture used serves to exaggerate this effect. Nevertheless, the advisability of comparing stress-strain measurements on films of approximately the same thickness, particularly in the early stages of aging, is apparent.

USE OF STRESS-STRAIN METHODS IN THE STUDY OF THE EFFECTS OF PLASTICIZERS AND SOLVENTS

Figure 20 represents curves obtained at different agings of films made up from the same base formula, the plasticizer and solvent content being varied as indicated. (Parts given in this formula and all succeeding ones are by weight.) The films all hardened progressively with age, the true plasticizers with the higher boiling points changing the least. The positions of the curves indicate the relative plasticizing power of the materials used, at the time the films were tested.

Figure 21 represents measurements of six films made from the same base formula but each containing a different plasticizer. The test specimens cut from these films were heated in an oven at 48°C. for the time noted in Figure 21 (a). The films were taken from the oven and allowed to come to room temperature before testing. Identical curves were obtained whether the heated films were allowed 15 minutes or 24 hours to come to room conditions.

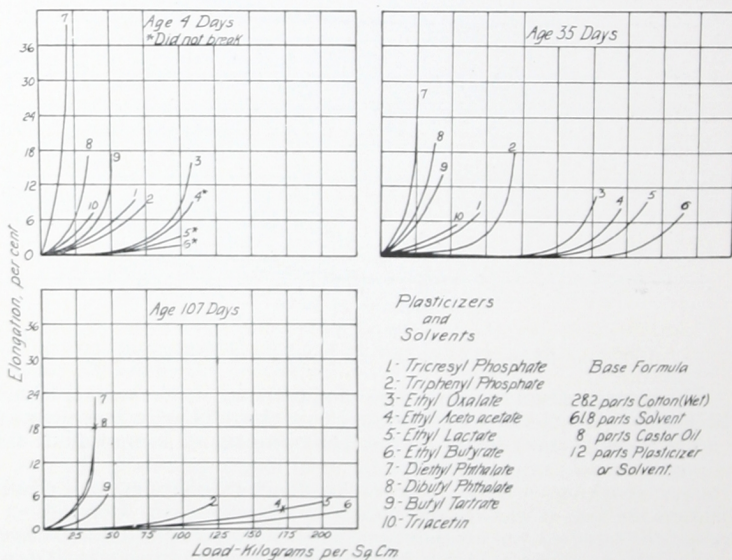


FIGURE 20
Characteristics Imparted by Various Plasticizers and Solvents (Natural Aging)

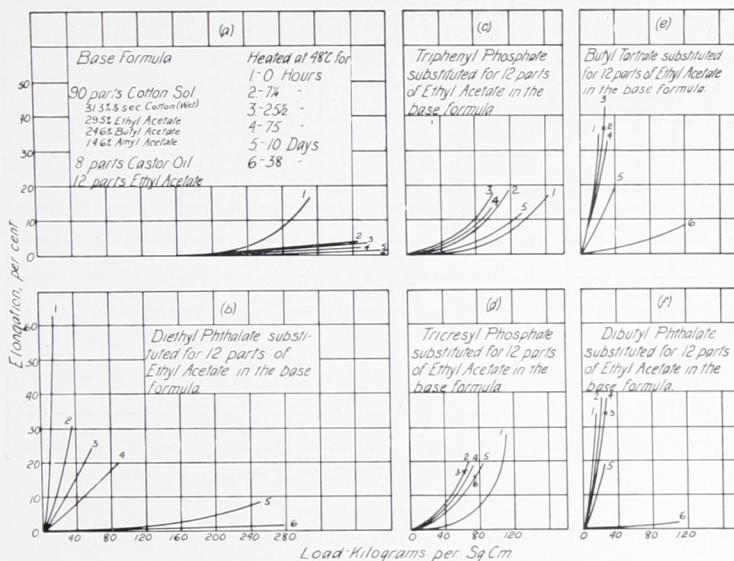


FIGURE 21
 The Effect of Slightly Accelerated Aging on a Few Plasticizers

The films containing the phosphates as plasticizers (c) and (d), softened at first on heating then became harder, while those containing the phthalates (b) and (f), butyl tartrate (e), and the one with no plasticizer (a), hardened progressively from the beginning. After 38 days' heating the film containing tricresyl phosphate was the softest, softer even than the original that had no heat treatment. The film containing triphenyl phosphate became very brittle with practically no elongation. This contrast in the behavior of triphenyl and tricresyl phosphates has been mentioned and discussed by Nelson and McKim.¹

¹Drugs, Oils and Paints, January, 1926; and Canadian Chemistry and Metallurgy, January, 1926.

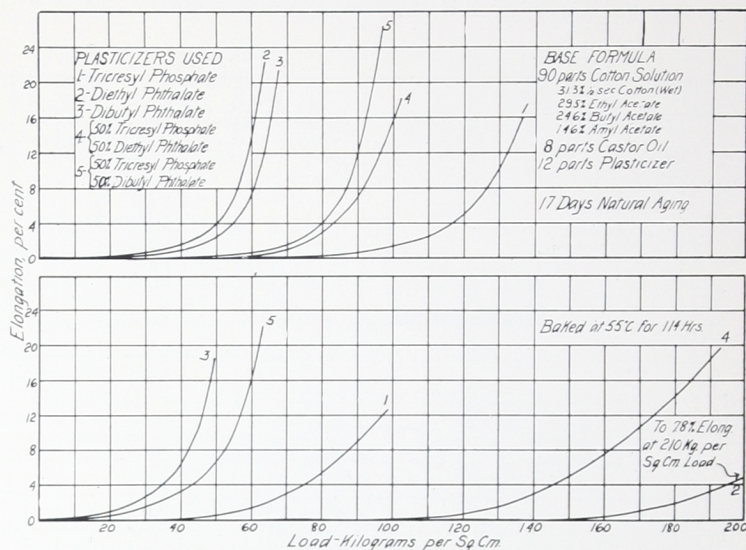


FIGURE 22
Plasticizers Used Singly and in Combinations

Figure 22 is a typical illustration of the use of stress-strain determinations in observing the effect of various combinations. The extreme range of changes in the physical properties of the film plasticized with diethyl phthalate alone is to be noted. At 17 days it is the softest film and after aging with heat (55°C.) becomes the most brittle. From a study of the curves it is apparent that under slightly accelerated aging conditions the phthalates carry over more of their individual characteristics, when used in combination with tricresyl phosphate, than does the latter.

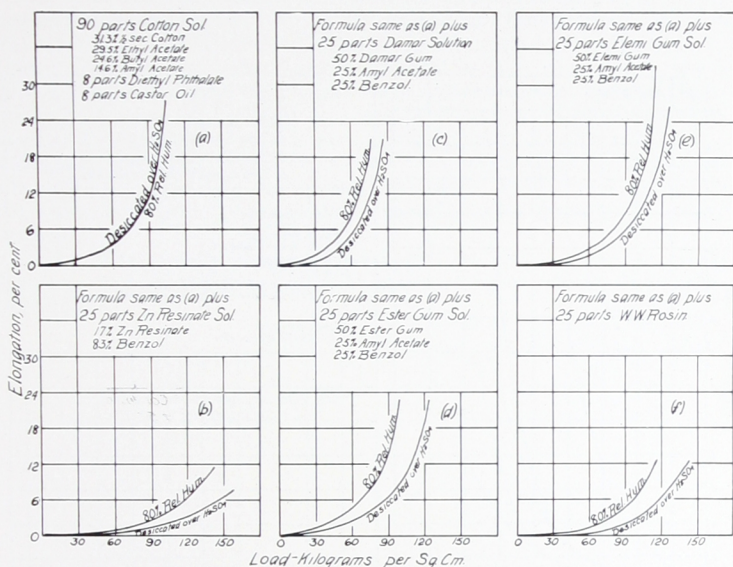


FIGURE 23
Characteristics Imparted by Various Resins

Resins

Figure 23 illustrates the effects imparted by five different resins. It will be noticed that the results on films containing no resin, Figure 23 (a) are the same at 80 per cent relative humidity as those desiccated. When, however, resins are introduced the film becomes more sensitive to moisture depending upon the kind and amount used.

In another series of curves (not shown) it was found that the acid number of ester gum was not a factor in film strength when the acid number of the gum varied from 7 to 20. In this series the specimens were aged for nine months and contained 13 parts of gum to 21 parts of dry cotton.

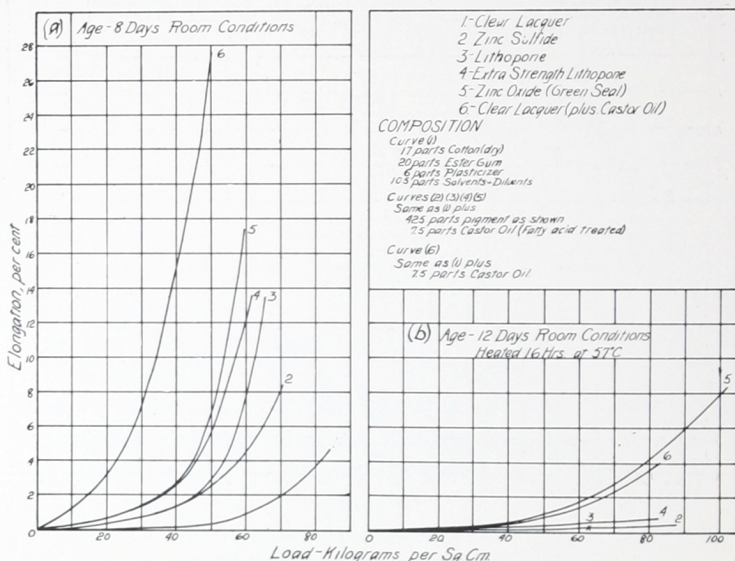


FIGURE 24
Characteristics Imparted by Four Different Pigments Under Slightly Accelerated Aging Conditions

Pigments

Figure 24 is a series representing the effect of equal weights of four representative pigments upon the distensible properties of a film. For comparison purposes two other curves are shown, the one being the clear lacquer, the other the clear lacquer plus the amount of castor oil introduced by the pigment pastes in the four pigmented films. The curves in Figure 24 (b) represent measurements taken after aging of the films at 57° C. for 16 hours. Under these conditions the clear lacquer film, No. 1, became too brittle for measurement.

The most striking feature of the curves is the fact that the incorporation of zinc oxide seems materially to extend the distensible life of the lacquer as reasoned from the curves. It is a recognized fact that the incorporation of zinc oxide in a clear lacquer will increase its life when exposed to ultra-violet light. However, it is to be remembered that in these experiments the films were not exposed except to ordinary room light conditions, so that the beneficial effect must be ascribed to some other cause. It might possibly be ascribed to a stabilizing action due to a ready neutralization of acid decomposition by-products, which are known to accelerate the decomposition of nitrocellulose, especially under slight heating. This argues for including zinc oxide with other pigments in lacquer formulas wherever it is feasible to do so.

The New Jersey Zinc Company will be glad to furnish complete drawings and plans for the apparatus described above, to those who are interested.



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